ATP-sponsored Workshop on Membrane/Separations Technologies
ATP 1999 National Meeting, November 17, 1999, San Jose, CA

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Overview

The theme and focus of this workshop was on technology barriers -- "What are the critical barriers and technology hurdles to wider application of membranes?" The cross-disciplinary and/or inter-disciplinary effort, which is required to make progress in new and emerging areas of membrane technology, proved to be an important sub-theme. A panel, composed of 10 experts, carefully chosen to represent the broad membrane technology community, and roughly equally divided between industrial scientists and academics, provided a clear agenda of issues to be discussed at the workshop. The edited and distilled pre-conference input, "Synopsis of Pre-Conference Commentary on Critical Issues and Barriers," provided as an appendix, served as a working document for the panel/audience discussion. The workshop benefited from the enthusiastic participation of some 60-70 experts, including the 10-member panel, drawn from widely diverse areas of membrane technology

Several invited talks preceded the panel discussion. Areas of membrane technology represented include polymeric and composite membranes for gas separations, inorganic (e.g., ceramic, carbon, molecular sieve) membranes, polymeric membrane systems for liquid separations, liquid membranes, membranes for fuel cell applications, and membranes for biomedical devices and for industrial biotechnology.

A substantial number of broad recommendations and a prioritized assessment of outstanding critical barriers emerged from the workshop. Emphasis was placed on new approaches that obviate existing barriers and enable step-ahead, game-changing technology. A critical barrier identified under cultural issues" – "Innovative research needs to be carried out in partnership with industrial producers and users" – communicates a broad perspective that is well aligned with the emphasis on teaming in the Advanced Technology Program. The full report from this workshop will be published early in 2000.

I. Presentations

"Limitation on Achievable Membrane Rejection Coefficient"
S. Mookie Sternberg, Baxter

The essential technical challenge in developing membranes for any separation process is the achievement of membrane transport properties that allow adequate passage of desired product while sufficiently hindering the passage of undesired components in the solution to be purified. The achievable rejection coefficient is ultimately limited by the presence of a small population of structures of any type, for example, pores through which the undesired components may pass. An analysis of transport mechanisms involved in porous membrane filtration was presented, which demonstrated the importance and effect of a few large pores or "defects" in achieving the desired rejection coefficient or, equivalently, the fractionation requirements during important separation applications.

“Desired Membrane Features for the 21st Century from the Industrial Perspective”
H. S. Muralidhara, Cargill, Inc., and David Paulson, Osmonics

The combined perspective of both an industrial user and a membrane manufacturer of pressure driven cross-flow membranes was represented in this presentation. Four critical requirements for a successful commercial application are: 1) integrity of the membranes and membrane systems within the application environment, 2) high selectivity, 3) acceptable throughput and 4) membrane cleanability. In addressing shortcomings of current membranes and membrane systems, emphasis must be placed on the integrated design of the entire system. Strong interdisciplinary efforts among materials and interfacial science and chemical engineering are required for the successful development of a new process, which, in turn, depends on the development of new materials with improved selectivity, transport, and fouling resistance. Anticipated future developments, including “smart,” e.g., autocleaning membranes, and hybrid membrane systems incorporating more than one unit operation in a membrane system were discussed.

“Ceramic Membranes - Unique Features and Needs”
Terry J. Mazanec, BP Amoco

This presentation highlighted the unusual materials and design requirements for high temperature ceramic membrane systems that can separate oxygen and simultaneously oxidize a (low value) light hydrocarbon such as methane. Novel process designs for ceramic membrane reactors that integrate oxygen separation and catalytic oxidation were discussed. Technical barriers were discussed in terms of four key areas – performance, fabrication, reliability, and reactor design – which are significantly interrelated. Key challenges in membrane and process design are maintaining membrane stability in the presence of 1) compositional expansion associated with oxygen uptake, and 2) steam corrosion under steady-state, start-up/shutdown, and transient conditions. Successful application of this new technology would comprise a game-changing step forward in industrial chemicals production.

II. Panel/Audience Discussion

Prior to the workshop the panel members (and a few other informed parties) submitted their initial thoughts on the question "What are the critical barriers and technology hurdles to wider application of membranes?" Individually, these responses varied in both detail and breadth but collectively covered a wide range of technical and non-technical membrane-related issues. A synopsis of these responses - "Synopsis of Pre-Conference Commentary on Critical Issues and Barriers" (see Appendix I) - was used as a working document by the panel and audience. This synopsis of responses was arranged into five broad categories:

1. Cultural Issues
2. Information/Knowledge Infrastructure
3. Membrane Process/Engineering/Manufacturing Systems Technology
4. Supporting Science and Engineering Knowledge
5. Membrane Material Properties

From the outset, the panel and participating audience took a broad view, identifying barriers which cut across many sectors of membrane technology. Emphasis was placed upon the need for new approaches in order to achieve desirable separation properties with materials that can be economically produced and in formats that provide process reliability. One panel member provided the following compact distillation of critical membrane barriers and hurdles (Note the interplay between several of the categories given above):

- ✯ Instability of economically-formable membranes under many practically important operating conditions
- ✯ Insufficient "interphase engineering" ability, which is needed to enable use of hybrid (organic-inorganic) materials and structures, a promising materials approach in the minds of several participants
- Coupling between the size and occurrence frequency of rate limiting "transport corridors" in selective layers; for example, both the pore size distribution in pressure-driven membrane filtration processes and the free-volume distribution in films used for gas and vapor separations, suffer from this issue.
- Coupling between support layer porosity and membrane pore size

But membrane technical innovations can have major hurdles to leap. An industry participant observed that, while this compact summary of critical barriers is a good one, a "step change" – one which is 30 to 50% cheaper – is needed to displace an existing separations process technology. Other participants suggested that cultural and process engineering issues, not merely economic ones, come strongly into play in the hurdle to establish a new membrane technology. A more detailed assessment of critical barriers in each of the five categories given above is provided in Section III.

A number of broad recommendations emerged from the workshop, including:

- Continue focus on materials
  - broaden definition of performance
  - include processability
- Importance of platform technologies (for example, moving toward a "universal" substrate)
- Emphasize understanding of the integrated system – Example: "Most membrane materials fail because we fail to understand pre-treatment."
- Development of accelerated stability tests
- View membranes as a tool – Example: Consider application of combinatorial methods to new membrane materials discovery and/or to understanding/addressing foulant

effects. (Two industrial participants indicated that they have practiced something close to this for addressing foulant effects.)

- Share internally-developed corporate information that is no longer of competitive value. Release of such information, already generally known among competitors, would facilitate wider application of the technology and prevent wasted research effort.
- New technology should be transparent, easy to use. (Such predictability of use to the end-user requires robust tests and attention to "plug and play.")
- Greater attention to cultural issues, particularly as these relate to embracing other disciplines and potential applications in non-traditional areas. A question paraphrased as – "Are we looking beyond ourselves for interaction and possible application in non-traditional disciplines?" – was accompanied by a recommendation to give presentations that are aimed at potential users in sessions outside those focused on membranes.

"Membrane technical innovations, essential to wider application of membrane technology, have major hurdles to leap," was the consensus message from this workshop. Strong emphasis was placed upon new approaches that obviate existing barriers and enable step-ahead, game-changing technology. Examples include: a high temperature proton exchange fuel cell utilizing new conductive membrane materials and electrolyte; a 'smart' polymer membrane that is electrically conductive (in which a voltage bias could modify pore size/shape); a membrane 'implant' that could aid in cleaning; and multi-functional membrane structures – especially inorganic, multi-functional structures for gas separation membranes and membrane reactors. These and other examples of new approaches are or are close to paradigm changes, consistent with a strong recommendation from one of the panel members for "out of the box" thinking. Such new materials and/or new process paradigms will drive different critical issues, as contrasted with incremental assaults on existing barriers.

New research approaches, particularly surface chemistry approaches and/or detailed interphase studies are needed to provide the science base for such new approaches. For example, the interphase engineering science issues at the nanoscale are not understood.

A prioritized assessment of outstanding critical barriers is provided in the following section.

III. Ranking of Critical Issues and Barriers

A core group of participants in the workshop's formal morning agenda met early in the afternoon of Wednesday, 11/17/99 in order to further discuss the morning's proceedings and to arrive at a ranking of the "critical issues and barriers" as summarized in the pre-conference synopsis (Appendix I).

In terms of the five broad categories from the pre-conference synopsis, the critical issues given priority are summarized below:

<u>Cultural Issues</u>

Highest priority-

- innovative research to be done in partnership with industrial producers and users

High priority-

- eliminate or minimize the repetition of pilot-scale demonstrations that are required in order to prove the robustness of the technology

Medium-to-low priority-

- overcome language and discipline barriers in order to facilitate interdisciplinary collaboration, and emerging technology in non-traditional areas (e.g., separations/ purification of genetic material, and specialty biomolecules)

Information/Knowledge Infrastructure

Highest priority-

- facilitate clear concise standards to relieve confusion caused by membrane producers with unique standards and evaluation approaches

High priority-

- share internally-developed corporate information that is no longer of competitive value. Release of such information, already generally known among competitors, would facilitate wider application of the technology and prevent wasted research effort.
- stimulation of public data collection, development of simulation software, and subsequent integration into commercial design toolboxes

Medium-to-low priority-

- foster membrane process 'job shops' not aligned with any manufacturer or technology
- facilitate the implementation of pre-existing open literature knowledge in technology development

Membrane Process/Engineering/Manufacturing Systems Technology

Highest priority-

- further develop improved membrane module designs (for example, better phase contactors; improved fluid mixing to avoid rate-limiting concentration boundary layers; designs that provide usefulness over a wider range of fluid properties - solids content, temperature, viscosity; and novel designs that facilitate internal staging for greater purification in a single device)

Medium priority-

- advance membrane material, element, and module manufacturing techniques -- with emphasis on addressing lack of reproducibility in membrane materials and reducing the impact of defects in process applications

Supporting Science and Engineering Knowledge

Highest priority-

- implement combinatorial or high-throughput screening methods for membrane material discovery
- develop predictive models to determine how a membrane's transport properties will change over time and exposure to complex feed mixtures (for example , the effects of fouling, plasticization, aging)

Medium-to-low priority-
- develop predictive models for transport of solute mixtures through porous and non-porous membranes

Membrane Material Properties
Highest priority-
- achieving higher conductivity, selectivity, and thermomechanical stability for membranes used in electrodialysis, water splitting, and fuel cells
- decreasing the dispersion in the physical pore size distribution for all pressure-driven membrane filtration materials, while maintaining or increasing overall productivity

Medium priority-
- Increase the selectivity of gas separation membranes over a broader temperature and trace contaminant range than is currently available (for example, extend operating temperature for selective gas and vapor separations into the 523-773 K range to enable hybrid processes)

Medium-to-low priority-
- Provide a broader range of solvent compatibility while retaining productivity and fractionating ability in liquid service.
- develop materials (both organic, inorganic, and mixed) that have both bulk and surface inertness, thus not changing their dimensions nor their surface energy over long term usage (for example, increased resistance to sorption leading to fouling)

Examples from "Specific Technology Wish List"
The workshop participants considered a number of examples from the "specific technology wish list." It was agreed that the list which follows, while certainly not exhaustive, illustrates specific examples of high priority:
- Stable liquid membranes and high capacity facilitated transport membranes.
- Functionalized membranes for chiral separations.
- Low cost solid polymer electrolytes
- New materials paradigm for fuel cell membranes – inorganic (high temperature) fast ion/proton conductors
- 3500 psi RO (reverse osmosis) modules
- Membranes for on-board fuel processing for transportation fuel cells.
- Membranes for separation of isomers, olefin-paraffin mixtures, and sulfur compounds from aromatics and saturates.

Conclusion

“Membrane technical innovations, essential to wider application of membrane technology, have major hurdles to leap,” was the consensus message from this workshop. A substantial number of broad recommendations and a prioritized assessment of outstanding critical barriers emerged from the workshop. Emphasis was placed on new approaches that obviate existing barriers and enable step-ahead, game-changing technology. With the exception of barriers in the category “Information/Knowledge Infrastructure,” the workshop’s assessment of ‘highest priority’ critical barriers comprises a broad-ranging array of high-risk technology hurdles that can be consistent with the objectives of the Advanced Technology Program. That is, proposals built upon high-risk technology challenges identified in the latter three categories (and giving due attention to the ATP criteria) would appear to be competitive. The highest priority Cultural Barrier identified – “Innovative research needs to be carried out in partnership with industrial producers and users” – communicates a broad perspective that appears to be well aligned with the emphasis on teaming supported by the Advanced Technology Program.

The results of this workshop also provide guidance for the broader basic science infrastructure supporting advances in membrane/separations technology. Certain of the technology barriers identified in this workshop are better addressed by agencies, such as NSF or DOE/Basic Energy Sciences, which fund high quality research programs in basic science and engineering. These include many of the barriers identified within Information/Knowledge Infrastructure and in Supporting Science and Engineering Knowledge and also in longer-range issues in Membrane Material Properties. In each of these categories, particularly the first, there appear to be “standards” issues in which NIST could play an important role in metrology advances. These observations bear testament to the broad perspective of the many assembled experts, industrial, academic and government, who contributed to this workshop.

Appendix I

Workshop on Membrane Separations Technologies
ATP 1999 National Meeting, November 15-17, 1999, San Jose, CA

Synopsis* of Pre-Conference Commentary on Critical Issues and Barriers

1. Cultural Issues

- Unless the membrane technology performs a unique and very profitable function, the “hurdle” for it to be adopted is higher than for other competitive approaches.
- Companies must be large enough to provide adequate insurance for possible losses in “mission critical” applications.
- Pilot-scale demonstrations are required in order to prove the robustness of the technology over and over again.
- Innovative research needs to be done in partnership with industrial producers and users.
- Discourage “over-funding” of unrealistic academic R&D and technology development efforts, as well as, “cheap thrills” applied research.
- Overcome language and discipline barriers --- in order to: 1) facilitate interdisciplinary collaboration, and 2) embrace/inculcate emerging technology in non-traditional areas, such as separations/purification of genetic material, specialty biomolecules.

2. Information/Knowledge Infrastructure

- Rate of knowledge growth seems to have exceeded the rate of its implementation in technology development.
- Facilitate the disclosure, accumulation, and organization of internal company information (including case studies) that no longer have confidential value -- this could accelerate progress in the research community.
- Stimulate public data collection, development of simulation software, and integration into commercial design toolboxes.
- Foster membrane process “job shops” that are not aligned with any manufacturer or technology.
- Early and “high-quality” training of students and new engineers to increase their familiarity with technology and the development of a variety of educational “resources”.
- Facilitate clear concise standards to relieve confusion caused by membrane producers with unique standards and evaluation approaches.

3. Membrane Process/Engineering/Manufacturing Systems Technology

- Further develop improved membrane module designs (e.g., contactors; fluid mixing; usefulness over a wider range of fluid properties - solids, temperature, viscosity; internal staging for greater purity).

- Advance membrane material, element, and module manufacturing techniques (address lack of reproducibility of membranes and impact of defects in process applications).
- Stimulate development of improved (more cost effective) pre-treatment and waste disposal equipment.
- Aid development of gentle, effective, and universal cleaning approaches to regenerate membrane modules (most important for liquid separations).

4. Supporting Science and Engineering Knowledge

- Predictive models to determine how a membrane's transport properties will change over time and exposure to complex feed mixtures (e.g., fouling, plasticization, aging).
- Properties and models of complex liquids (e.g. colloids) at interfaces and in bulk solutions.
- Predictive models for transport of solute mixtures through porous and non-porous membranes.
- Combinatorial methods for membrane material discovery.

5. Membrane Material Properties

- Decrease the dispersion in the physical pore size distribution (the ideal being monodispersity) for all pressure-driven membrane filtration materials, while maintaining (or increasing) overall productivity.
- Size exclusion for organic-organic separations with good discriminating power between species with less than an order of magnitude size difference.
- Broader range of solvent compatibility while retaining productivity and fractionating ability in liquid service.
- Develop materials (both organic, inorganic, and mixed) that have both bulk and surface inertness, thus not changing their dimensions nor their surface energy over long term usage (e.g., fouling).
- Decouple trade-off between productivity from selectivity in gas and vapor separating materials.
- Increased selectivity of gas separation membranes over a broader temperature and trace contaminant range than is currently available (e.g., extend operating temperature for selective gas and vapor separations into the 523-773 K range to enable hybrid processes).
- Higher conductivity, selectivity, and thermomechanical stability for membranes used in electrodialysis, water splitting, and fuel cells.

6. Examples From The "Specific" Technology Wish List

- Stable liquid membranes and high capacity facilitated transport membranes.
- Functionalized membranes for chiral separations.
- Low cost solid polymer electrolytes
- New materials paradigm for fuel cell membranes – inorganic (high temperature) fast ion/proton conductors
- 3500 psi RO (reverse osmosis) modules
- Membranes for on-board fuel processing for transportation fuel cells.

- Membranes for separation of isomers, olefin-paraffin mixtures, and sulfur compounds from aromatics and saturates.

*This list is a distillation of the comments received from ~12 membrane technologists in response to the question “What are the critical barriers and hurdles to wider application of membranes?” The full comments will be reorganized and made available as an appendix in the final report of this workshop. This synopsis was prepared with the objective of helping the panel to more quickly reach consensus on issues, prioritize barriers, and suggest some specific mechanisms for overcoming them.

Appendix II

Panel Members – Workshop on Membrane/Separations Technologies, ATP 99 National Meeting, November 17, 1999, San Jose, CA:

Dr. H. S. Muralidhara, Cargill, Inc.
David Paulson, Osmonics
Dr. S. Mookie Sternberg, Baxter
Dr. Paul Bryan, MIT
Professor William J. Koros, University of Texas at Austin
Dr. Terry Mazanec, BP Amoco
Professor W. S. Winston Ho, University of Kentucky
David Furukawa, Pres., Separation Consultants, Inc.
Dr. Subhash Narang, SRI International
Professor Kamalesh K. Sirkar, NJIT